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Keywords: Carbon membrane, Surface flow, Gas separation

1. Introduction

Petroleum refineries are among the largest users of hydrogen in the chemical industry. Hydrogen is used in hydrogenation, desulfurization and denitrogenation processes and a large source of hydrogen in refining operations is the production of aromatic compounds which are used as octane enhancers in gasoline. Environmental regulations are requiring refiners to reduce the amount of aromatic compounds in transportation fuel and, thus, the total amount of hydrogen produced in dehydrogenation processes is being reduced. In addition, refineries are being forced to use crudes which are higher in sulfur which further increases the total H_2 needs. This requires refiners to make or buy hydrogen by conventional methods such as Steam-Methane Reforming or to recover hydrogen from their processes. The purpose of this paper is to describe the preparation and performance of a new carbon-based gas separation membrane and its application in two new processes for hydrogen recovery from refinery waste streams.

2. Selective Surface Flow TM Mechanism

Surface diffusion on nanoporous membranes is an attractive choice for practical separation of gas mixtures because the separation selectivity is determined by preferential adsorption of certain components of the gas mixture on the surface of the membrane pores, as well as by selective diffusion of the adsorbed molecules [1]. The Selective Surface Flow (SSFTM) mechanism is shown schematically in Figure 1 for a mixture of hydrogen and hydrocarbons. The hydrocarbons are more strongly adsorbed on the pores than hydrogen on the high-pressure side of the membrane. These adsorbed components diffuse along the pore surface to the low-pressure side of the membrane where they desorb into the permeate stream. If the pores of the membrane are made small, the adsorbed layer of hydrocarbons serves to block the gas phase flow of hydrogen across the pore. Thus, the feed gas is depleted in the hydrocarbons and an enriched hydrogen stream is withdrawn at feed pressure. This is in contrast to typical polymeric membranes which selectively permeate hydrogen. Permeation selectivities of these membranes can be very high because the adsorption selectivity is high even at low feed pressure. The hydrocarbon permeability across the membrane will be high because the diffusivity for surface diffusion is orders of magnitude higher than typical diffusivities for these components through a polymeric matrix. This allows the membrane thickness to be 1-3 microns rather than the submicron membrane thicknesses typically needed for polymeric membranes. We have developed a novel nanoporous carbon-based membrane which exhibits these properties and shows very attractive gas separation properties for hydrogen/hydrocarbon and carbon dioxide/methane/hydrogen mixtures.

3. Membrane Preparation

We have prepared very thin, defect-free, nanoporous carbon membranes by converting a thin-film of polyvinylidene chloride polymer to carbon by pyrolysis. A polyvinylidene chloride (PVDC) latex (55 wt% solids) was cast on a porous graphite support; the film thickness was estimated to be between 5 and 10 microns. The coated support was then carbonized to temperatures between 600 and 1000°C under nitrogen to convert the PVDC to carbon. This coating and carbonizing procedure was repeated up to five and the resultant carbon layer had a thickness of 1-3 microns.

Permeation properties of the carbon membrane were measured using a plate and frame membrane module. A schematic representation of the module is shown in Figure 2. It can hold 6 flat sheet carbon membranes to provide a total membrane area of ~0.5 ft². The purge gas passed through the module countercurrent to the feed direction. The module was instrumented to allow measurement of feed and effluent gas flows and compositions.

The pore size of the membrane was estimated by comparing the pure methane diffusivity through the membrane to the methane diffusivity through zeolites of known pore structure [1]. It was found that methane diffusivity through the carbon membrane is in the activated diffusion regime

and the mean pore size is ~ 5.5 Å. This suggests that these membranes will exhibit the Selective Surface Flow properties.

4. Practical Applications of SSF™ Membranes

4.1 Recovery of Hydrogen From Refinery Fuel Gas

Refinery waste streams are typically used as fuel within the plant. They contain 20-50% H_2 and C_1 - C_4 hydrocarbons are available at pressures of 50 to 150 psig. Conventional separation methods are not amenable to hydrogen recovery from these streams because of low hydrogen recovery efficiency or high energy of separation. Pressure swing adsorption (PSA) process are commonly used in hydrogen separation and purification, however, the overall hydrogen recovery is low when the feed gas contains hydrogen concentrations less than ~ 50 -60% [2]. Additionally, hydrogen PSA systems cannot handle C_4 + hydrocarbons because these constituents are not easily desorbed from the adsorbent. Polymeric membranes are used in refineries for hydrogen recovery however they typically require high feed gas pressure (>300 psig) and they produce hydrogen at the low pressure side which requires recompression before being fed to a PSA system [3]. The use of two compression steps (feed and permeate) make this process very energy intensive.

A process to recover a good portion of the H_2 from such mixtures without further compression of the feed gas while rejecting a substantial portion of the hydrocarbons and has been patented by Air Products and Chemicals, Inc. [4]. The refinery waste gas is fed to an SSF™ carbon membrane module at the available pressure. The H_2 -enriched stream on the high pressure side of the membrane can then be compressed and separated in a conventional pressure swing adsorption (PSA) process to produce ultra-pure H_2 . The waste gas from the PSA system containing some H_2 and lower hydrocarbons can be used to provide the low-pressure purge stream for the membrane. Figure 3 shows a schematic flow sheet for such a membrane-PSA hybrid scheme.

The performance of the carbon membranes for separation of a multicomponent H_2 -hydrocarbon mixture was tested in plate-and-frame membrane module. A gas mixture containing 40.9% H_2 , 20.2% CH_4 , 19.8% C_2H_6 , 9.2% C_3H_8 and 9.9% C_4H_{10} (mole %) at 50 psig was used as the feed gas and a purge gas consisting of H_2 , CH_4 and C_2H_6 mixtures (typical PSA waste of Figure 3) was passed through the module in a countercurrent direction to the feed gas flow. The module was operated at $-11.0^\circ C$ and $25^\circ C$. It was found that the membrane could be used to produce a H_2 -enriched gas containing 56.0% H_2 while rejecting (to the lower pressure side) 100.0% C_4H_{10} , 92.0% C_3H_8 , 67.5% C_2H_6 and 36.0% CH_4 . The H_2 recovery in the membrane was 63.0%. The H_2 -rich gas was produced at 48 psig from the membrane unit (see Figure 3). These membrane clearly show Selective Surface Flow properties --- high rejection of heavier hydrocarbons and high hydrogen recovery at feed pressure.

The hydrocarbon-rich membrane reject gas could be used as fuel. The recovered H_2 -rich gas from the membrane could be further compressed to a pressure of 200 psig and fed to a conventional PSA system in order to produce a 99.99+% H_2 product with an overall H_2 recovery of $\sim 43.0\%$ from the waste feed gas. Thus, the nanoporous membrane can be used to recover a valuable chemical (H_2) from a waste gas using only one compressor between the high pressure effluent and the PSA system.

A comparison of the relative energy requirement for recovering H_2 by this process and to make hydrogen using conventional Steam-methane reforming shows that the membrane/PSA hybrid process requires 15% energy less than reforming [6].

4.2 Enhanced Hydrogen Recovery in Hydrogen Manufacture

Steam Methane Reforming (SMR) followed by separation of the reformer product (typically 75% H_2 , 20% CO_2 , 4% CO , and 1% CH_4) in a pressure swing adsorption (PSA) system is the method of choice for H_2 manufacture today. The reject stream from the PSA (5 psig) contains a significant amount of hydrogen (approximately 20% of the PSA feed) which is used as fuel for the reformer (See Figure 4). The H_2 in PSA reject stream cannot be economically recovered by conventional technology because the hydrogen concentration and pressure are low.

SSF™ membranes have the advantage of operating very efficiently even at low pressures. These membranes can be used to increase the overall hydrogen recovery of the SMR/PSA process by recovering and recycling part of the hydrogen from PSA reject gas. A schematic diagram of the process patented by Air Products and Chemicals, Inc. [5] is shown in Figure 5. The reject of the PSA is compressed from 5 to 30 psig. An SSF™ membrane module is then used to selectively remove CO_2 , CO and CH_4 and enrich the hydrogen. The enriched hydrogen product from the membrane can be compressed and recycled to the PSA unit. A countercurrent CH_4 sweep gas is used on the low-pressure side of the membrane at 3 psig.

The performance of the SSF™ membranes for separation of CO₂ and CH₄ from H₂ was measured at 294K using a feed gas containing 35% H₂, 55% CO₂, and 10% CH₄. It was assumed that CO behaves similar to CH₄. The feed pressure was maintained at 30 psig and a low-pressure CH₄ sweep gas used at a flowrate of 15% of the feed flowrate and pressure of 3 psig. Under these conditions, the membrane was able to reject 87.5% of the CO₂, 64.3% of the CH₄ while recovering 55% of the H₂.

The overall hydrogen recovery from a SMR/PSA system shown in Figure 5 was calculated using the above membrane performance. The membrane selectively rejects the CO₂, CO and CH₄ thereby reducing the flow of the recycle stream to the PSA feed and enriching the H₂ concentration. The addition of the recycle does not significantly change the PSA feed composition so that the PSA H₂ recovery remains constant. The overall hydrogen recovery for this process was 89.9% compared to a hydrogen recovery of 80% for the base case without the SSF membrane. This significant improvement in H₂ recovery is only possible because the SSF™ membrane can be operated efficiently at such low feed-gas pressure.

5. Summary

A novel microporous carbon membrane has been developed that uses adsorption and surface flow as the means of gas separation. These membranes have significant advantages in terms of energy efficiency and overall process performance for the separation of H₂ from refinery waste gas streams compared to conventional methods.

6. References:

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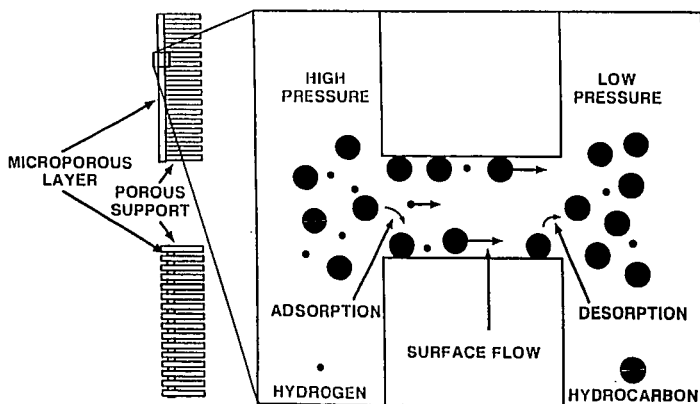


Figure 1: Mechanism of Gas Separation by Selective Surface Flow

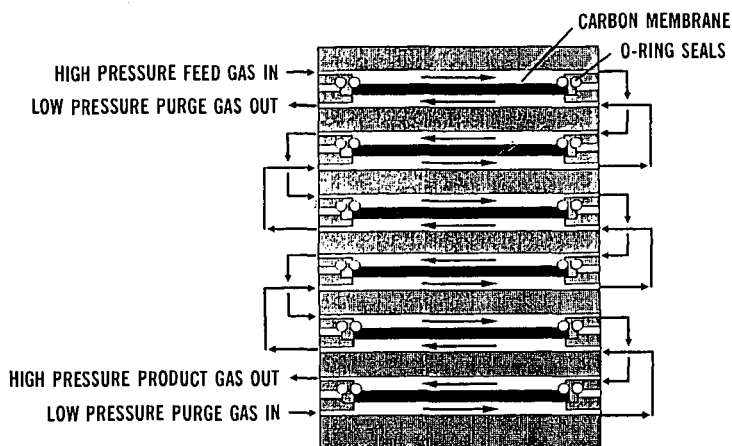


Figure 2: Plate-and-Frame Membrane Module

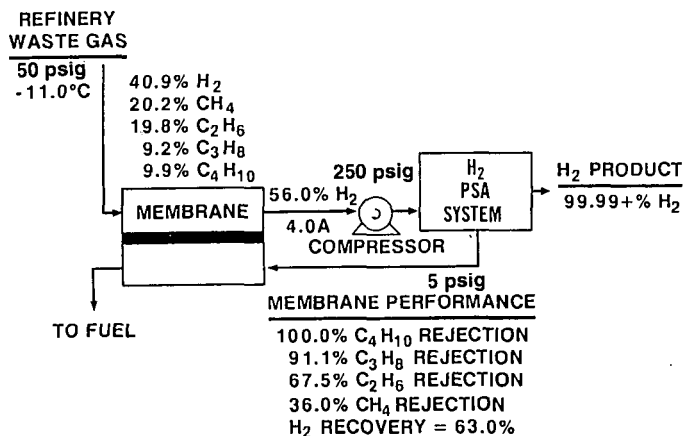


Figure 3: Process for Recovery of H_2 from Refinery Waste Streams

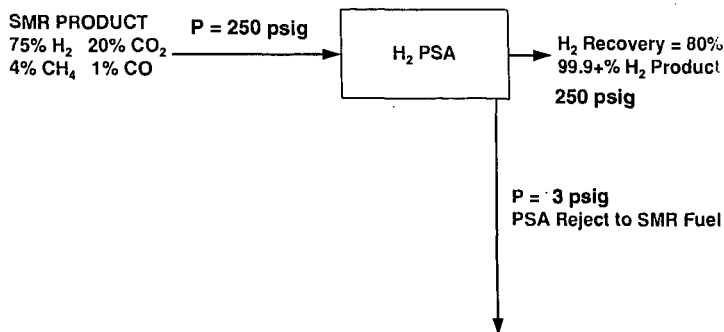


Figure 4: Conventional Process for H_2 Production

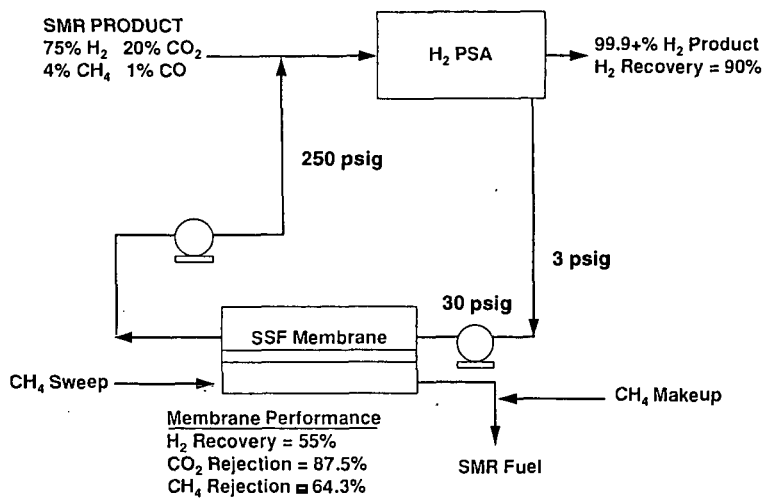


Figure 5: Enhanced H₂ Production using SSF Membranes